

Occurrence and Distribution of MTBE and Gasoline Hydrocarbons in Ground Water and Ground Water Used as Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993-2002

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Abstract

The occurrence of MTBE and gasoline hydrocarbons was examined in two national-scale surveys, one for ground water and one for source water, and one regional-scale survey of drinking water. The overall detection frequency of MTBE in all three surveys was similar to the detection frequencies of some other VOCs that have much longer production and use histories in the United States. When the data for ground water and source water were limited to the same geographic extent as drinking water data, the detection frequencies of MTBE in ground water and source water were comparable to the detection frequency of MTBE in drinking water. In all three surveys, the detection frequency of any gasoline hydrocarbon was less than the detection frequency of MTBE. No concentration of MTBE in source water exceeded the U.S. Environmental Protection Agency's Drinking-Water Advisory of 20 µg/L, only one concentration of MTBE in ground water exceeded 20 µg/L, and only 0.9 percent of drinking-water samples exceeded 20 µg/L.

The overall detection frequency of MTBE relative to other widely used VOCs indicates that MTBE is an important concern with respect to protection of ground-water resources. Ground water from public-supply wells and shallow ground water underlying urban land-use areas has a greater probability of MTBE contamination compared to ground water from domestic wells and ground water underlying non-urban land-use areas. Areas with higher population density, areas where MTBE is used as a gasoline oxygenate, and areas with higher recharge have a greater probability of MTBE contamination of ground water.

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Introduction

The Clean Air Act (CAA) Amendments of 1990 specified that oxygen must be added to gasoline in areas where air-quality standards have not been attained (U.S. Environmental Protection Agency 1990). Oxygenates are compounds that contain oxygen and are added to gasoline in order to meet the requirements of the CAA Amendments. For about a decade now, oxygenates have been used in gasoline in areas regulated under the Reformulated Gasoline (RFG) and Oxygenated Fuel (Oxyfuel) Programs of the CAA Amendments. As of 1998, approximately 30 percent of all gasoline in the United States contained oxygenates for compliance with RFG requirements and an additional 4 percent containing oxygenates for compliance with Oxyfuel requirements (U.S. Environmental Protection Agency 1998).

Although the CAA Amendments did not specify which oxygenate must be added to gasoline in these areas, the alkyl ether methyl-tertiary butyl ether (MTBE) has been, and continues to be, the most commonly used oxygenate. As of 1998, MTBE was used in more than 80 percent of oxygenated gasoline. Recent information indicates that MTBE is currently the most frequently used gasoline oxygenate in RFG areas (U.S. Environmental Protection Agency 2003a) while ethanol is currently the most frequently used gasoline oxygenate in Oxyfuel areas (U.S. Environmental Protection Agency 2003b). In addition to its use as a gasoline oxygenate, MTBE also has been widely used to enhance octane in gasoline (U.S. Environmental Protection Agency 1998).

Since about 1991, large volumes of MTBE have been produced every year in the United States and used as a gasoline oxygenate. In 2001, production of MTBE in the United States was over 12 billion liters (Department of Energy 2002). From 1993 to

1998, MTBE was the second most-produced organic chemical in the United States (U.S. Environmental Protection Agency 1998).

A chemical with such large production and widespread use has a substantial potential of release to the environment. Once released to the environment, MTBE can be transported to ground-water resources through a variety of mechanisms. Once in ground water, MTBE concentrations can adversely affect the quality of water from aquifers that are used to supply water for private household wells or public water-supply systems. MTBE has also been found in some reservoirs and rivers that are used as public water supplies (Grady 2003).

MTBE in drinking water may have possible human health consequences including carcinogenic and detrimental reproductive and developmental effects (Hartley and others 1999). Intake of MTBE by gavage has been associated with acute and long-term (carcinogenic) health effects in laboratory animals (Robinson et al. 1990; Belpoggi et al. 1995). In 1997, the U.S. Environmental Protection Agency issued a drinking-water advisory recommending that MTBE concentrations in drinking water be below the range of 20 to 40 µg/L (micrograms per liter) to protect consumer acceptance (taste and odor) and also to provide a large margin of safety from toxic effects (U.S. Environmental Protection Agency 1997). The U.S. Environmental Protection Agency is continuing to assess the human health effects of MTBE and the implications of setting a drinking water standard.

MTBE has been detected in ground water in the United States and other countries such as Germany (Moran, Clawges, and Zogorski 2002; Moran, Lapham, Rowe, and Zogorski 2002; Klinger et al. 2002). Recent data show the presence of MTBE in ground

water used as a source for drinking water (Grady 2003) and in drinking water in the U.S. (Grady and Casey 2001; Williams et al. 2002). Contamination of ground water used as a source for drinking water already has resulted in the closure of many drinking-water wells around the country including both public and private wells.

Research has shown that detections of MTBE in ground water are more frequent in areas where MTBE is used as a gasoline oxygenate, such as RFG or Oxyfuel areas, in comparison to areas where it is not used as a gasoline oxygenate (Moran, Clawges, and Zogorski 2002). However, MTBE also has been detected in ground water in many other areas of the Nation outside of the RFG and Oxyfuel areas. The geographically widespread detection of MTBE indicates that ground water in many areas may be at potential risk of MTBE contamination (Moran, Clawges, and Zogorski 2002).

The purpose of this report is to examine the occurrence of MTBE and gasoline hydrocarbons in ground water, source water, and drinking water from data collected or compiled by the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program and cooperators. In this report, gasoline hydrocarbons refer to a select group of VOCs whose primary use is believed to be in gasoline and includes the BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds as well as naphthalene, *n*-butylbenzene, *iso*-propylbenzene, styrene, and 1,2,4-trimethylbenzene. Although these VOCs are components of gasoline, they do have other domestic, commercial and industrial uses and they may have other sources to ground water apart from gasoline.

This report provides an overview for the entire Nation of occurrence of MTBE in ground water and ground water that is withdrawn for human consumption prior to any treatment (hereafter referred to as source water). The occurrence of MTBE in drinking

water in 12 Northeast and Mid-Atlantic States also is examined. The focus of this report is on the occurrence, distribution, and concentrations of MTBE and gasoline hydrocarbons in these media, and on the occurrence of MTBE in areas where MTBE content in gasoline is used as a surrogate for MTBE input to the environment. This report also examines other factors that are associated with the occurrence and behavior of MTBE in ground water and that may aid in understanding the sources and pathways of MTBE to ground water and the vulnerability of aquifers to MTBE contamination.

Data and Methods

Data were analyzed from three surveys: 1) the NAWQA Program that sampled ground water throughout the United States from 1993-2002 as a part of occurrence studies (ground-water survey), 2) a collaborative effort of the NAWQA Program and other organizations in a national survey that sampled ground water used as a source of drinking water throughout the United States from 1999-2000 (source-water survey), and 3) the NAWQA Program that compiled data on drinking water from community water systems (CWSs) in 12 Northeast and Mid-Atlantic States that were sampled from 1993-1998 (drinking-water survey).

As part of NAWQA occurrence studies, personnel collected samples of ground water between 1993 and 2002. These samples were analyzed for MTBE and other volatile organic compounds (VOCs) at the USGS National Water-Quality Laboratory (NWQL). The ground-water occurrence studies of NAWQA included two main components: 1) large-scale studies of water quality in one or more aquifers underlying each NAWQA study area, and 2) land-use studies assessing the quality of ground water

underlying agricultural and urban land-use areas (Gilliom et al. 1995). In the large-scale studies, NAWQA personnel sampled large areal and depth dimensions of a principal aquifer that constitutes an important ground-water resource within a study area. In the land-use studies, NAWQA personnel sampled shallow ground water in areas of predominant agricultural or urban land use (Gilliom et al. 1995). Sampling in the land-use studies was designed to target recently recharged ground water generally less than 10 years old.

The design for each of the NAWQA occurrence studies was network-based consisting of the selection of about 30 wells (sampling sites) in an unbiased, random, equal-area distribution throughout the study area. The wells sampled by NAWQA were not located in close proximity to known point source releases. As of January 2003, data on MTBE were available for 3,964 wells sampled in the NAWQA occurrence studies that constitute the ground-water survey.

Personnel from CWSs throughout the United States collected samples of ground water used as a source of drinking water from 1999 to 2000 as part of a national source-water survey. This survey was a collaborative effort between the American Water Works Association Research Foundation (AWWARF), the Metropolitan Water District of Southern California (MWDSC), the Oregon Health and Sciences University, participating CWSs, and the USGS. The purpose of this survey was to assess the magnitude and spatial extent of MTBE contamination of source water whether derived from surface water or ground water. In this report, only source water from ground water was considered. Two phases of the national source-water survey, with respect to ground water, were accomplished: 1) a random survey of 571 ground-water sources throughout

the country, and 2) a focused survey of 80 ground-water sources throughout the country that were considered more susceptible to MTBE contamination (Clawges et al. 2001). Detailed results of both the random and focused surveys can be found in Grady (2003) and Delzer and Ivahnenko (2003), respectively. In this report, only data from the random survey were used in order to avoid potential bias in the occurrence of MTBE.

The selection of CWSs sampled in the random survey was statistically based and was stratified by population-served size category, source of water (ground water or surface water), and total number of people served (Ivahnenko et al. 2001). For ground water, all source-water samples were collected prior to treatment and as close as possible to the wellhead. The MWDSC laboratory analyzed the samples of source water from the random survey for MTBE and other VOCs. Data on MTBE and other VOCs were available from a total of 571 samples of ground water that constitute the source-water survey.

Data on MTBE and other VOCs in drinking water were compiled by the USGS from various agencies in 12 Northeast and Mid-Atlantic States. Unlike the previous ground-water and source-water surveys, the drinking-water survey was not national in scope and only covered these regions. The purpose of this survey was to describe the occurrence and distribution of MTBE and other VOCs in public drinking water supplied by CWSs in these regions. These regions were selected because they generally are densely populated, have a long-term history of urbanization, and are areas with high use of public-water supply (Grady and Casey 2001; Moran et al. 2001). In addition, large parts of these regions are regulated under the RFG Program. A random subset of all

CWSs in the regions was selected using a statistical approach that stratified selection by State, source of water, and number of people served (Grady and Casey 2001).

Data from the 12 Northeast and Mid-Atlantic States represent drinking water that was sampled to meet the requirements of the Safe Drinking Water Act (SDWA). The samples were collected from 1993-1998 and were analyzed by a variety of State and private laboratories. The data on drinking water does not reflect occurrence by source but instead is summarized by system. A CWS was counted as having a detection of MTBE if a measurable concentration of MTBE was reported in one or more water samples associated with any source or sample location for that CWS. In this report, only samples of drinking water obtained from ground-water sources were used for analysis. Data on MTBE and other VOCs were available for a total of 985 CWSs with ground-water sources that constitute the drinking-water survey (Grady and Casey 2001).

Laboratory reporting levels varied between the surveys and also within two of the surveys. For ground water collected by NAWQA, variability in the laboratory reporting level for MTBE primarily was the result of the introduction of new, information-rich methods and a change in the policy of NWQL concerning the determination of laboratory reporting levels (Rose and Schroeder 1995; Connor et al. 1998; Oblinger Childress et al. 1999). NWQL laboratory reporting levels for MTBE in ground-water samples ranged from 0.1 µg/L to 1.66 µg/L with a median of 0.17 µg/L. NWQL laboratory reporting levels above 0.2 µg/L may be the result of dilution of environmental samples or laboratory censoring of data after review of laboratory quality control (QC) information.

For source-water samples analyzed by MWDSC, the laboratory reporting level for MTBE was constant at 0.078 µg/L. However, review of field QC data indicated

extensive low-concentration contamination of field and trip blanks by various VOCs. As a result, all source-water environmental samples were censored at a level of 0.2 µg/L for all VOCs to ensure that reported concentrations represent environmental concentrations of VOCs and not systematic contamination.

For drinking-water samples, the laboratory reporting level for MTBE ranged from 0.1 µg/L to 10 µg/L with a median of 0.5 µg/L. The variability in reporting levels in this data set primarily was a result of different censoring criteria and instrument performances of the various State and private laboratories that performed the analyses. Criteria for inclusion of drinking-water data in this analysis included the collection of field QC data to ensure that a minimum standard of data quality was maintained. It was required that QC data be used to evaluate and, if necessary, to censor drinking-water data to ensure that reported concentrations represent environmental concentrations of VOCs and not systematic contamination (Grady and Casey 1999).

Field QC data collected by the NAWQA Program indicated that systematic contamination of environmental samples by MTBE resulting from collection, processing, handling, and shipping did not occur (G.C. Delzer, U.S. Geological Survey, 2002, oral commun.). For gasoline hydrocarbons, field QC data indicated several samples in which systematic contamination was suspected. Samples that had suspected systematic contamination were coded (D.A. Bender, U.S. Geological Survey, 2002, oral commun.) and were not used in this analysis.

In all three surveys, each well, source, or sampling site was allowed to have only one set of environmental data representing a time snapshot of water quality. In cases where more than one set of environmental water-quality results was available, the most

recent set was selected. Therefore, each well, source, or sampling site had only one set of water-quality results. Consequently, the term “sample” is used in this report to indicate the results from a single well, source, or sampling site.

Assessment Level Computations

Data analysis was complicated by the variations in laboratory reporting levels between the surveys. In order to accurately compare detection frequencies of MTBE and gasoline hydrocarbons between different data sets that have varying reporting levels, it was necessary to apply a uniform censoring level that is referred to here as an assessment level. If a water-quality constituent has reporting levels that vary between data sets, comparisons of detection frequencies between the data sets may not reflect true differences in water quality. Instead, they may simply reflect differences in instrument sensitivity, analytical methods, or censoring levels between the different laboratories.

For comparing the detection frequencies of water-quality constituents with varying laboratory reporting levels, an assessment level should be applied before detection frequencies are computed. The application of an assessment level allows for the most accurate comparison of detection frequencies between different data sets with different laboratory reporting levels.

In this report, an assessment level of 0.2 µg/L was applied whenever MTBE detection frequencies were compared between the three surveys. However, if comparisons of detection frequencies were made between subsets of a single survey, or detection frequency was examined wholly within a single survey, no assessment level was applied. To execute the assessment level, analyses with a detectable concentration

less than 0.2 µg/L were converted to non-detections. Detection frequency was then computed as the number of samples that had a detected concentration of MTBE greater than or equal to 0.2 µg/L divided by the number of samples with MTBE analyses times 100.

For comparisons of MTBE concentrations between the three surveys, an assessment level of 0.5 µg/L was applied to data for ground water and source water to make the data most comparable to the drinking-water data. This level was chosen because the median laboratory reporting level for data from the drinking-water survey is 0.5 µg/L and there are no concentrations below this level in this data set.

Statistical Methods

To better understand the significance of results and the hydrologic processes that have caused them, statistical tests were performed to evaluate and compare data. The statistical significance level (α) used here for all tests was 0.05. The results of some statistical tests are shown graphically on the figures as letter symbols. If two groups of data share the same letter symbol, the null hypothesis was not rejected for that comparison. If two groups of data do not share the same letter symbol, the null hypothesis was rejected for that comparison.

Contingency table tests, using Pearson's chi-square test of independence, were performed to determine if detection frequencies between one or more surveys, or detection frequencies between subsets of one survey, were independent. Contingency table tests were used because detection frequencies are nominal, categorical variables. The null hypothesis states that the row variables are independent from the column

variables. If the null hypothesis is rejected, the row variables are dependent on the column variables and the detection frequencies were considered dependent on the survey.

The nonparametric Mann-Whitney test was used to compare two independent groups of data such as the population densities around wells between areas of high and low MTBE use in gasoline. The null hypothesis states that the values in one group are higher than the values in the other group. If the null hypothesis is rejected, the values in one group are higher than the values in the other group.

The nonparametric Kolmogorov-Smirnov test was used to compare MTBE concentrations between surveys in order to determine if the distributions of concentrations were significantly different. The null hypothesis states that the distributions are not significantly different. If the null hypothesis was rejected, the distributions were considered significantly different.

For determining associations between multiple independent variables and MTBE occurrence, a multivariate logistic regression analysis was used (Helsel and Hirsch 1992). For water-quality analyses, the independent variables selected for analysis are often anthropogenic or are hydrogeologic parameters that can provide insight and understanding into the sources, transport processes, or environmental mechanisms that influence or affect contamination. In water-quality analyses, logistic regression often is used to predict the probability of occurrence of a contaminant as it relates to various independent variables. However, in this case the regression results were not intended to provide a capability for predicting the probability of detecting MTBE. The regression results only were used to determine associations between MTBE occurrence and independent variables and to determine the strength and direction of the associations.

For individual independent variables, if the Wald statistic p -value of the slope coefficient was less than 0.05 and the upper and lower bounds of the odds ratio did not include 1, the variable was considered significantly associated with the probability of occurrence of MTBE. For the overall regression equation, the null hypothesis was rejected if the overall likelihood ratio of the model produced a p -value of less than 0.05, in which case all independent variables were considered significantly associated with the probability of occurrence of MTBE. The significance of non-nested regression analyses was tested using Akaike's Information Criteria (Helsel and Hirsch 1992). Standardized coefficients were used to compare the strength of a relation between the dependent variable and different independent variables. They indicate how many standard deviations of change in the dependent variable are associated with one standard deviation of change in the independent variable (Menard 2002). The method for computing standardized estimated coefficients followed Menard (2002).

Occurrence and Concentrations of MTBE and Gasoline Hydrocarbons

The geographic distribution of samples analyzed for MTBE in all three surveys is shown in figure 1. The circles in figure 1 represent the locations where samples were collected. The open circles show the location of samples that did not have a detected concentration of MTBE, whereas the dark circles show the location of samples that had a detected concentration of MTBE. In this case, no assessment level was applied to the data in order to illustrate the number and location of all detected MTBE concentrations. In all three surveys combined, 420 samples had detected concentrations of MTBE using no assessment level. This corresponds to an overall detection frequency of 7.6 percent in

a total of 5,520 samples. Samples with a detected concentration of MTBE are most intensively represented in the Northeast region of the country (fig. 1).

Occurrence of MTBE

The detection frequency of MTBE in each of the three surveys is illustrated in figure 2. Data for ground water and source water were analyzed at an assessment level of 0.2 µg/L to make them most comparable to data for drinking water. For ground-water (NAWQA) data, the detection frequency is only for MTBE analyses in the large-scale studies because this is the best representation of the quality of the ground-water resource. The bold letters in figure 2 graphically display the results of chi-square tests of independence comparing MTBE detection frequencies between the three surveys.

The detection frequency of MTBE was lowest in ground water at 2.9 percent and highest in drinking water at 9 percent (fig. 2). The detection frequency of MTBE in source water was 5.4 percent. The results of the contingency tables tests indicated that the detection frequencies of MTBE were dependent on the survey with p -values < 0.05 for all comparisons.

In order to make the data most comparable to drinking water, ground-water and source-water data also were examined in only the 12 Northeast and Mid-Atlantic States and at an assessment level of 0.5 µg/L. For ground water, the detection frequency of MTBE in these regions was 6.6 percent, whereas the detection frequency of MTBE in source water from these regions was 11.3 percent. These detection frequencies were similar to the detection frequency of MTBE in drinking water. In this case, the results of the contingency tables tests indicated that the detection frequencies of MTBE were not dependent on the survey with p -values > 0.05 for all comparisons.

Occurrence of Gasoline Hydrocarbons

The detection frequency of any gasoline hydrocarbon in each of the three data sets also is illustrated in figure 2. Data for ground water and source water were analyzed at an assessment level of 0.2 µg/L to make them most comparable to data for drinking water. Gasoline hydrocarbons are defined in this report as VOCs that are NAWQA target analytes and whose primary use is believed to be in gasoline. They include the BTEX (benzene, toluene, ethylbenzene, and xylenes) compounds as well as naphthalene, *n*-butylbenzene, *iso*-propylbenzene, styrene, and 1,2,4-trimethylbenzene. Although these VOCs are components of gasoline, they do have other domestic, commercial and industrial uses and they may have other sources to ground water apart from gasoline. The bold italics letters in figure 2 graphically display the results of chi-square tests of independence comparing the detection frequencies of gasoline hydrocarbons between the three surveys.

The detection frequency of any gasoline hydrocarbon was lowest in drinking water and highest in source water (fig. 2). For ground water and drinking water, the detection frequency of any gasoline hydrocarbon was less than the detection frequency of MTBE. However, the detection frequency of any gasoline hydrocarbon in source water was slightly higher than the detection frequency of MTBE (fig. 2). The results of the contingency tables tests indicated that the detection frequencies of any gasoline hydrocarbon were not dependent on the survey between ground water and drinking water ($p > 0.05$; 2×2 contingency table) but were dependent on the survey between source water and ground water and between source water and drinking water ($p < 0.05$; 2×2 contingency tables).

Individually, gasoline hydrocarbons were detected less frequently than MTBE in all three surveys. In source water, the detection frequencies of individual gasoline hydrocarbons were highest. However, gasoline hydrocarbons were detected in less than 4 percent of source-water samples, with toluene being detected most frequently in 3.5 percent of samples. In ground water and drinking water, the detection frequencies of any individual gasoline hydrocarbon were even less, with no compound found in more than 2 percent and 1 percent of samples, respectively. Like source water, the most frequently detected gasoline hydrocarbon was toluene detected in 1 percent of samples from ground water and in 0.6 percent of samples from drinking water.

Occurrence of MTBE in NAWQA Studies

As indicated previously, NAWQA also conducts land-use studies of shallow ground water in areas of predominant agricultural or urban land use. Figure 3 illustrates the detection frequencies of MTBE in the large-scale studies, land-use studies, and all studies combined using no assessment level. The detection frequency of MTBE was highest in urban land-use studies at 13 percent and lowest in agricultural land-use studies at 1.2 percent. The detection frequency of MTBE in the large-scale studies was intermediate at 2.8 percent. For all of NAWQA studies combined, the detection frequency of MTBE was 4.7 percent.

For various studies of ground-water quality, the NAWQA program samples many different types of wells. Figure 4 illustrates the detection frequencies of MTBE in four different types of wells sampled by the NAWQA Program using no assessment level. Although domestic-supply wells are most frequently sampled by NAWQA for MTBE,

the detection frequency of MTBE is highest in monitoring wells compared to all other types of wells.

Occurrence of Benzene

An important aspect of the RFG Program is the limitation of benzene in reformulated gasoline to less than or equal to 1 percent by volume (U.S. Environmental Protection Agency 1990). Normally gasoline contains between 1 and 1.5 percent benzene by volume. Although gasoline in the Oxyfuel Program areas is not required to have a 1-percent benzene limitation, the high content of MTBE required by the Oxyfuel Program (15 percent by volume) probably results in the displacement of other fuel components such as benzene. This means that gasoline in areas of high MTBE use should contain less benzene relative to areas of low MTBE use, and detection frequencies and concentrations of benzene should be lower in areas of high MTBE use relative to areas of low MTBE use.

A examination of data from ground water indicated that the detection frequency of benzene was higher in areas of low MTBE use (4.7 percent) relative to areas of high MTBE use (2 percent) when no assessment level was applied and the detection frequency of benzene was dependent on MTBE use ($p < 0.05$; 2×2 contingency table). However, the distributions of concentrations of benzene were not different between areas of high and low MTBE use ($p > 0.05$; Kolmogorov-Smirnov test).

Occurrence of Other Ethers

Besides MTBE, the NAWQA Program analyzed for three other alkyl ethers that have been used commercially as gasoline oxygenates (Zogorski et al 1997). These compounds were analyzed in both the NAWQA ground-water survey and the source-water survey and include: *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), and ethyl *tert*-butyl ether (ETBE). In ground water at an assessment level of 0.2 µg/L, only two of the three ethers were detected: TAME and DIPE. The detection frequencies of both of these compounds were less than MTBE and were detected in less than 1 percent of samples. TAME was detected in 0.25 percent of samples (6 of 2,382 samples), whereas DIPE was detected in 0.19 percent of samples (4 of 2,077 samples). The fewer number of ground-water samples that were analyzed for ethers as compared to MTBE resulted from these compounds not being analyzed by the NWQL until April 1996. In source water, all three ethers were detected at least once at an assessment level of 0.2 µg/L. Like ground water, the detection of any of these ether compounds in source water was considerably less than the detection of MTBE. Both TAME and DIPE were detected in only 0.3 percent of source-water samples (2 of 579 samples), whereas ETBE was detected in only one sample.

Concentrations of MTBE

Concentrations of MTBE in each of the three surveys are illustrated in figure 5. In this figure, the data from ground-water survey include only MTBE concentrations from the large-scale studies. An assessment level of 0.2 µg/L was used to make ground-water data comparable to source-water and drinking-water data. However, in ground water many detections of MTBE were below 0.2 µg/L. Of all the detections of MTBE in

ground water, 38 percent (113 of 300) were less than 0.2 µg/L. One reason for the numerous low-level detections in ground water was the information-rich reporting conventions employed by the NWQL for analysis of VOCs in water. The information-rich method used for analyzing VOCs allows for reporting of concentrations below both the laboratory reporting level and long-term method detection limit (Oblinger Childress and others, 1999). It has been demonstrated that as the level of detection of a VOC is lowered, the frequency of detection in ground water increases (Moran, Lapham, et al. 2002).

Similar to detection frequencies, the median detected MTBE concentration was lowest in ground water and highest in drinking water. Using an assessment level of 0.2 µg/L, median concentrations were 0.67 µg/L in ground water, 0.71 µg/L in source water, and 1.8 µg/L in drinking water. For ground water, only one sample had a detected concentration above 20 µg/L, which is the lower limit of the U.S. Environmental Protection Agency's Drinking-Water Advisory (U.S. Environmental Protection Agency 1997). For source water, no detected MTBE concentration exceeded 20 µg/L. For drinking water, nine samples (0.9 percent) had detected MTBE concentrations above 20 µg/L. The samples with concentrations of MTBE in drinking water that exceeded the lower limit of the advisory were collected in the following states: Connecticut (2), New York (3), Rhode Island (1), and Virginia (3).

A statistical comparison was made of the MTBE concentrations between each of the three surveys. The results are shown by the letter symbols in figure 5. The results of the statistical analyses indicate that the distributions of MTBE concentrations between ground water and drinking water were significantly different ($p < 0.05$; Kolmogorov-

Smirnov test), but the distributions of concentrations between ground water and source water and between source water and drinking water were not significantly different ($p > 0.05$; Kolmogorov-Smirnov test). Quantile-quantile plots indicated that the concentrations of MTBE in drinking water were higher than the concentrations of MTBE in either ground water or source water.

Use of MTBE in Gasoline as a Surrogate for Environmental Input

To understand the occurrence of MTBE in the environment, it would be ideal to know the exact location and amount of all releases of MTBE to the environment. At a national scale, such knowledge is impossible to identify or ascertain. However, releases of MTBE to the environment are undoubtedly related to the amount of MTBE used in gasoline. Use of MTBE in gasoline in various areas of the country can be estimated in several ways. One way of estimating use is by considering areas previously or currently under the RFG Program, and where MTBE is used as the gasoline oxygenate, as being areas where high amounts of MTBE are used.

Further refinement and specificity in determining MTBE use can be obtained using information from gasoline surveys. Several surveys have been conducted to provide information on the physical properties and constituents of gasoline including octane number, specific gravity, and volumes of olefins, aromatics, benzene, alcohols, and various ether oxygenates. The surveys provide information on MTBE content in gasoline, in percent by volume, for areas that are included within the surveys. The purposes of these surveys are to provide comparative information on gasoline

composition to companies interested in the physical and chemical properties of fuels and to verify that oxygen content in gasoline is sufficient to meet RFG and Oxyfuel Program requirements. Additional information on these surveys can be found in Moran, Clawges, and Zogorski (2002).

Samples from the three surveys were placed into two groups based on the above information: 1) relatively high MTBE use, and 2) relatively low MTBE use or unknown MTBE use. A sample was designated as being from an area of relatively high MTBE use if either: 1) the sample was located in an area that was designated for RFG usage at any time from 1993 to 2001 and where MTBE was used as the gasoline oxygenate, or 2) the sample was located in an area where gasoline surveys indicated a long-term average for MTBE content in gasoline, from 1990-1999, of greater than or equal to 3 percent by volume. If either 1 or 2 were not true for a sample, or if the MTBE use of the area where the sample was located was unknown, the sample was coded as being from an area of relatively low MTBE use. Using this categorization scheme, each sample was placed into a category of high or low MTBE use.

Detection frequencies of MTBE within areas of high and low MTBE use for each survey are presented in figure 6. Data for ground water and source water were analyzed at an assessment level of 0.2 µg/L to make them most comparable to data for drinking water. For NAWQA data, the detection frequency is only for MTBE analyses in the large-scale studies because this is the best representation of the quality of the ground-water resource. The letters above each bar represent the results of chi-square tests of independence for each survey between areas of high and low MTBE use. The numbers

between the arrows represent the ratios of detection frequencies between areas of high and low MTBE use.

For each survey the detection frequency of MTBE was higher in areas of high MTBE use compared to areas of low MTBE use. For each survey, the detection frequencies of MTBE were dependent on MTBE use ($p < 0.05$; 2×2 contingency tables). The ratios of detection frequencies between areas of high and low MTBE use varied from 4.9 for drinking water to 7.5 for ground water. This indicates that the detection frequency of MTBE was about 5 to 7.5 times higher in areas of relatively high MTBE use compared to areas of relatively low MTBE use. When comparing between the surveys in areas of either high or low MTBE use, the detection frequencies of MTBE were dependent on the survey ($p < 0.05$; 2×3 contingency tables).

Research has shown that the probability of detecting MTBE at or above $0.5 \mu\text{g/L}$ in ground water is related to population density (Squillace and Moran 2000). An analysis was performed for this report to determine if the detection frequency of MTBE is related to population density. In order to control for MTBE use, a comparison was made of the detection frequencies of MTBE between areas of high and low population density for areas of high and low MTBE use. For this analysis, only data from ground water were used because the data for source water had too few detections to provide a meaningful comparison and the data for drinking water were too limited in geographic extent to provide a good overall national distribution. Population density is related to areas of urban and non-urban land use. Areas with population densities less than 50 people/km^2 (square kilometer) can be classified as non-urban, whereas areas with population densities greater than 50 people/km^2 can be classified as urban (Hitt 1994). This land-use

classification scheme was used to place all samples within a land use category of either urban or non-urban.

Detection frequencies of MTBE in ground water between urban and non-urban land-use areas and areas of high and low MTBE use are presented in figure 7. No assessment level was applied in determining detection frequency in ground water in figure 7 because no comparison was made to other data sets. The numbers between the arrows represent the ratios of detection frequencies between urban and non-urban areas. When controlling for MTBE use, the detection frequency of MTBE in ground water was clearly related to population density as indicated by urban and non-urban land use (fig. 7). The ratios of detection frequencies between urban and non-urban land-use areas were similar between areas of MTBE use. Also, the detection frequency of MTBE in non-urban areas of high MTBE use was similar to the detection frequency of MTBE in urban areas of low MTBE use. The above indicate that population density is an important factor affecting the occurrence of MTBE.

A comparison was made of the concentrations of MTBE in ground water between areas of high and low MTBE use. In order to make the comparison most equitable, the effect of population density on MTBE concentrations was considered. Based on the previous analyses, only samples with a population density of greater than or equal to 50 people/km² were selected. Thus, a comparison of the concentrations of MTBE in urban land-use areas for areas of high and low MTBE use was made. Figure 8 is a quantile-quantile plot of MTBE concentrations in ground water for urban land-use areas and between areas of high and low MTBE use. Because the data are solely for ground water, no assessment level was applied. For construction of the quantile plot, non-detections

were given an arbitrary value of 0.001 µg/L for plotting purposes. Each point on figure 8 represents the MTBE concentration in each data set corresponding to a specific quantile. For simplicity, the quantile pairs of non-detections are not shown on figure 8. All data pairs with both concentrations above 0.001 µg/L plot above the 1:1 line indicating higher concentrations of MTBE in areas of high MTBE use relative to areas of low MTBE use (fig. 8). A Kolmogorov-Smirnov test indicated that the distributions of MTBE concentrations were significantly different between areas of high and low MTBE use ($p < 0.05$).

MTBE and Dissolved Oxygen in Ground Water

An analysis of MTBE occurrence under oxic and anoxic ground-water conditions was performed. Oxic ground water is defined in this report as ground water that contains greater than 0.5 mg/L of dissolved oxygen, whereas anoxic ground water is defined as ground water that contains less than or equal to 0.5 mg/L of dissolved oxygen. Freeze and Cherry (1979) indicated that natural ground water is considered oxidized if it has a pE value above 13.4, which is approximately equal to a dissolved oxygen value of 0.5 mg/L. In this report only samples of ground water were used because dissolved oxygen information was not available for either source-water or drinking-water data. In order to control for MTBE use, only samples from high MTBE use areas were examined.

When no assessment level was applied, the detection frequency of MTBE in oxic ground water was higher at 24.5 percent than the detection frequency of MTBE in anoxic ground water at 22.5 percent, but the detection frequencies of MTBE were not dependent

on dissolved oxygen conditions ($p > 0.05$; 2×2 contingency table). An analysis of MTBE concentrations and dissolved oxygen, both as continuous variables, indicated that there was not a monotonic relation between the two variables when non-detections were included in the analysis and no censoring was applied ($p > 0.05$; Spearman correlation).

However, when only higher concentrations of MTBE were considered by applying various assessment levels to the data, the detection frequencies of MTBE in oxic and anoxic ground water were different. When an assessment level of $0.2 \mu\text{g/L}$ was applied to MTBE concentrations, the detection frequency of MTBE in oxic ground water was lower at 14.1 percent than the detection frequency of MTBE in anoxic ground water at 18.3 percent; however, the detection frequencies of MTBE were not dependent on dissolved oxygen conditions ($p > 0.05$; 2×2 contingency table). When an assessment level of $0.5 \mu\text{g/L}$ was applied to MTBE concentrations, the detection frequency of MTBE in oxic ground water was lower at 7.6 percent than the detection frequency of MTBE in anoxic ground water at 14.8 percent. In this case, the detection frequencies of MTBE were dependent on dissolved oxygen conditions ($p < 0.05$; 2×2 contingency table). When censoring was applied to MTBE concentrations at an assessment level of $0.5 \mu\text{g/L}$, a significant monotonic relation was found between MTBE concentrations and dissolved oxygen ($\rho = -0.119$; $p < 0.05$; Spearman correlation).

Other Associations With MTBE Occurrence in Ground Water

Associations between MTBE occurrence and various hydrogeologic and anthropogenic variables were examined using multivariate logistic regression. For the logistic regression analyses, only data from ground water were used because hydrogeologic and anthropogenic information was scarce or not available for data from the source-water and drinking-water surveys. The dependent or response variable was the detection of MTBE, and no assessment level was applied to the MTBE data because no comparison was made to other data sets. Table 1 lists the independent variables that were used for these analyses, the units for each variable, the coding of the variable in the logistic regression analyses, and the source of the data. Prior to analysis, population density was transformed using a natural logarithm function to normalize the distribution.

Table 2 summarizes the results of the logistic regression analyses for the independent variables that were significantly associated with MTBE occurrence, the unstandardized estimated coefficients, the standardized estimated coefficients, and the odds ratios. The independent variables found to be significantly associated with the probability of detecting MTBE in ground water included: population density, use of MTBE in gasoline, recharge, aquifer consolidation, soil permeability, and the density of leaking underground gasoline storage tanks (table 2). Population density, the use of MTBE in gasoline, and the density of leaking underground gasoline storage tanks in the vicinity of the sampled well represent anthropogenic influences and help to approximate input of MTBE to the environment.

Population density was found to be most strongly associated with the probability of detecting MTBE as indicated by the standardized coefficient for population density in

table 2. This means that an increase in population density results in the greatest increase in the probability of detecting MTBE when controlling for the other significant independent variables. Use of MTBE in gasoline also was strongly associated with the probability of detecting MTBE. When controlling for the other significant independent variables, the probability of detecting MTBE was about 5.8 times higher in high MTBE use areas compared to low MTBE use areas, as indicated by the odds ratio for use of MTBE in table 2. Although the density of leaking underground gasoline storage tanks in the vicinity of the sampled well also was associated with the probability of detecting MTBE in ground water, the effect of this variable on the probability of occurrence was much smaller relative to population density and use of MTBE in gasoline (table 2).

The other variables significantly associated with the probability of detecting MTBE in ground water included recharge, aquifer consolidation, and soil permeability (table 2). These variables represent hydrogeologic conditions that influence or affect the transport and fate of MTBE in the environment. Recharge is the hydrogeologic variable that was found to be most strongly associated with the probability of detecting MTBE in ground water. The probability of detecting MTBE in ground water increases as recharge increases. Although aquifer consolidation and soil permeability also were associated with the probability of detecting MTBE in ground water, the effect of these variables on the probability of occurrence was much smaller relative to recharge. The probability of detecting MTBE in ground water is higher in aquifers composed of consolidated material compared to aquifers composed of unconsolidated material. As soil permeability increases, the probability of detecting MTBE in ground water also increases.

Sources of MTBE

Most of the MTBE used in the United States is for oxygenation of gasoline. Thus, the release of gasoline is the primary method for MTBE entering the environment. Besides gasoline, used motor lubricating oil, home heating oil, and diesel fuel also have been identified as containing MTBE and releases of these products also could be possible sources of MTBE (Baker et al. 2002; Robbins et al. 1999; 2000). Some potential non-point sources of MTBE include evaporative losses from tanks or pipelines, incomplete combustion in engines, urban storm-water runoff from areas with small spills, exhaust from motorized watercraft with incomplete combustion or leaks from watercraft tanks, overfilling spills, and small (non-reportable) consumer releases of either domestic, commercial, or industrial origin. Some potential point sources of MTBE to the environment include leaks from large domestic or commercial gasoline, diesel fuel, heating oil, or waste oil storage tanks and associated piping (underground and aboveground), leaks from transport pipelines or bulk stations, larger overfilling spills, motor vehicle or truck accidents, and large consumer releases.

It has been hypothesized that MTBE concentrations greater than 20 µg/L in ground water are the result of point source releases (Moran et al. 1999). However, certain intense non-point sources of MTBE, such as atmospheric concentrations around certain parking garages, gas stations, or roadways, could result in MTBE concentrations of up to 30 µg/L in shallow ground water through atmospheric deposition (Squillace et al. 1997). Nonetheless, it would be unusual for non-point sources to cause such high concentrations in ground water. Low concentrations of MTBE, on the other hand, could have either point or non-point sources. Very few samples analyzed in the three surveys

had concentrations of MTBE greater than 20 µg/L. This indicates that very few samples had MTBE concentrations that can be confidently attributed to point sources.

Another line of evidence to support the hypothesis that higher concentrations of MTBE are from point sources can be found by examining the occurrence of MTBE with other gasoline hydrocarbons. In general, MTBE did not occur frequently with gasoline hydrocarbons in the three surveys. In all data sets combined and at an assessment level of 0.2 µg/L, MTBE occurred in a total of 307 samples and gasoline hydrocarbons occurred together with MTBE in only 28 of these samples (9 percent). However, when MTBE concentrations were divided into categories reflecting relatively low, medium, and high concentrations, a pattern in the occurrence of gasoline hydrocarbons and MTBE together became apparent (fig. 9). For relatively low (0.2 to 1 µg/L) and medium concentrations of MTBE (1 to 20 µg/L), the occurrence of gasoline hydrocarbons at an assessment level of 0.2 µg/L was less than 10 percent. For relatively high MTBE concentrations (greater than 20 µg/L), the occurrence of any gasoline hydrocarbon was substantially higher at 41 percent (fig. 9). Although the number of samples represented by high MTBE concentrations in figure 9 is small, the trend in the data is quite clear. As concentrations of MTBE increase, the occurrence of gasoline hydrocarbons with MTBE increases. This supports the contention that higher concentrations of MTBE are from point sources.

Discussion and Implications

The overall detection frequency of MTBE for all three surveys combined was less than 10 percent using no assessment level. One explanation for this relatively low national detection frequency may be that large quantities of MTBE have been used only relatively recently in oxygenated gasoline and the use of oxygenated gasoline has been highly regionalized. Drinking water in the Northeast region of the country appeared to have the highest intensity of MTBE detections among the three surveys. This region is an area of substantial current and former use of oxygenated gasoline, has a long-term history of dense urbanization and high population, and may be an area of greater aquifer vulnerability.

The overall detection frequency of MTBE for all three surveys, at 7.6 percent, was higher than the detection frequency of trichloroethene (4.5 percent) and lower than the detection frequency of tetrachloroethene (11.9 percent). Both trichloroethene (TCE) and tetrachloroethene (PCE) have much longer production histories than MTBE and both have been produced and used in the United States since 1923 (Pankow and Cherry 1996). MTBE has only been produced substantially since about 1970, although production of MTBE in the United States has outpaced both TCE and PCE since about 1980 (Johnson et al. 2000). Consequently, it is surprising to find the detection frequency of MTBE rivaling or surpassing these VOCs that have been produced and used for much longer periods of time. This indicates that MTBE contamination is an important concern with respect to the protection of ground-water resources.

MTBE in Drinking Water

The detection frequency of MTBE was higher in drinking water in the Northeast compared to the national surveys of source water or ground water. The higher detection frequency of MTBE in drinking water may be related to: 1) the data on drinking water are only for public-supply wells, which generally have large pumping capacities, 2) the detection frequencies in drinking water may be biased high because the Northeast and Mid-Atlantic regions are areas of high MTBE use, and 3) the data on drinking water did not reflect occurrence by specific source but instead was summarized by system with any detection of MTBE in any one or more water samples associated with any source or sample location in a system constituting a detection for that system.

Because the drinking-water data were exclusively from public-supply wells, a higher detection frequency of MTBE might be expected as public-supply wells generally have higher pumping rates and larger areas contributing recharge to the well than other well types such as private-supply wells (domestic) and monitoring wells (Moran, Lapham, et al. 2002). Stackelberg et al. (2000) found that the number and total concentrations of VOCs per sample were significantly higher in ground water from public-supply wells compared to monitoring wells in the surficial Kirkwood-Cohansey aquifer system in southern New Jersey. The larger volumes of water withdrawn from public-supply wells compared to monitoring wells and the subsequently larger contributing areas were believed to be responsible for intercepting more ground water flowing from VOC point sources (Stackelberg et al. 2000). Bruce and Oelsner (2001) found that the water quality of closely located domestic and public-supply wells with respect to pesticides were not similar and that public-supply wells had a higher detection frequency of pesticides. They attributed the higher detection frequency of pesticides in

public-supply wells to the higher pumping rate and seasonal pumping cycles of these wells that produced more recently recharged water near the water table containing more anthropogenic compounds.

Another factor that may have contributed to a higher detection frequency of MTBE in public-supply wells is their location in the Northeast and Mid-Atlantic regions where substantial use of oxygenated gasoline has occurred and where MTBE was the primary oxygenate. In areas of substantial use of MTBE, an increased probability of release of MTBE to the environment and transport to ground water exists.

Finally, the data on MTBE in drinking water were summarized by system and this may have resulted in a bias towards a higher detection frequency because many systems had multiple sources with multiple samples (Grady and Casey 2001). In fact, when the detection frequency of MTBE for drinking water was computed for both ground and surface water sources relative to the number of samples, rather than the number of systems, it was lower at 6.2 percent (Grady and Casey 2001).

When the data for ground water and source water were limited in extent to only the 12 Northeast and Mid-Atlantic States and an assessment level of 0.5 µg/L was applied, the detection frequencies of MTBE in ground water and source water were comparable to the detection frequency of MTBE in drinking water. Because these regions have large areas with high use of MTBE in gasoline, this indicates that the occurrence of MTBE in ground water, source water, and drinking water is similar when controlling for use of MTBE.

MTBE Occurrence Land Use and Well Type

For ground water, the detection frequency of MTBE was highest in urban land-use studies compared to the large-scale studies or agricultural land-use studies. The higher detection frequency of MTBE in urban land-use studies probably is a result of several factors: 1) these are areas of highest population density and thus highest gasoline use, 2) highly urban regions like the Northeast and parts of California have most intense use of MTBE in gasoline, and 3) the urban land-use studies targeted shallow ground water in urban areas and were designed to sample recently recharged ground water generally less than 10 years old. Thus, shallow ground water underlying urban land-use areas is at greater risk of contamination by MTBE.

For ground water, the detection frequency of MTBE was highest in monitoring wells compared to other well types. The higher detection frequency of MTBE in monitoring wells is due to several factors: 1) monitoring wells were used extensively in the urban land-use studies, and 2) many monitoring wells were installed by NAWQA for land-use studies and were shallow in depth, designed to sample recently recharged ground water near the top of the water table. Although NAWQA sampled fewer public-supply wells compared to domestic wells, the detection frequency of MTBE in public-supply wells was higher. As mentioned, the detection frequency of many VOCs has been shown to be higher in public-supply wells compared to domestic wells for several reasons. Because public water-supply systems served over 100 million people as of 2001 and 91 percent of systems used ground water as the primary water source (Farrelly 2002), the potential of exposure to MTBE from ground-water contamination is large.

MTBE Concentrations

The median detected MTBE concentration in ground water and source water was less than 1 µg/L, and the median detected MTBE concentration in drinking water was less than 2 µg/L. These relatively low concentrations indicate that many of the MTBE detections could be from non-point sources or that point sources have not caused widespread areas of high-level concentrations near the sampled wells. No samples of source water exceeded the lower limit of the U.S. Environmental Protection Agency's Drinking-Water Advisory. The incidence of MTBE concentrations exceeding the lower limit of the advisory relative to all samples was quite low for both ground water and drinking water. Thus, most of the ground water and drinking water analyzed in this report did not contain MTBE concentrations that would cause organoleptic effects.

However, the potential long-term human health effects of low-level concentrations of MTBE by consumption of water are not well understood. To be protective of carcinogenic potential and reproductive and developmental effects, maximum levels of MTBE in drinking water ranging from 5 µg/L to 100 µg/L have been suggested (Johnson 1998; Hartley et al. 1999). The California Department of Health Services has issued a Maximum Contaminant Level for MTBE in drinking water of 13 µg/L based on the observed carcinogenic effects of MTBE in experimental animals (California Department of Health Services 2002). The U.S. Environmental Protection Agency is continuing to study the implications of MTBE contamination for human health (Davis 2002). Considering the current level of concern regarding the health effects of MTBE and the continuing uncertainty in this area, monitoring of drinking water for MTBE is still recommended.

In this report, higher concentrations of MTBE ($> 20 \mu\text{g/L}$) are believed to result from point sources of contamination. When the concentration of MTBE was considered, the occurrence of any gasoline hydrocarbon together with MTBE was substantially increased for higher concentrations of MTBE. This indicates that the source of higher concentrations of MTBE is a point source such as a leaking underground storage tank or pipeline because other gasoline hydrocarbons are associated with MTBE in the same sample. Low concentrations of MTBE ($< 20 \mu\text{g/L}$) probably are the result of an unknown mix of point and non-point sources. Additional research is needed to better understand the sources of low concentrations of MTBE.

Gasoline Hydrocarbon Occurrence

For ground water and drinking water, the detection frequencies of any gasoline hydrocarbon or individual gasoline hydrocarbons were less than the detection frequency of MTBE. The lower detection frequencies of gasoline hydrocarbons compared to MTBE are believed to be a result of differences in transport and fate properties between the different compounds. MTBE has higher water solubility than gasoline hydrocarbons. MTBE adsorbs only weakly to subsurface solids, whereas gasoline hydrocarbons adsorb relatively strongly. As a result, MTBE moves at velocities that are similar to the velocities of local ground water while the velocities of gasoline hydrocarbons are retarded relative to the velocities of local ground water (Squillace et al. 1997). In addition, the aerobic half-life of MTBE in ground water has been estimated to be approximately an order of magnitude longer than the average aerobic half-life of the BTEX compounds in ground water (Howard et al. 1991). Aerobic half-lives in ground water were chosen for comparison because approximately 70 percent of NAWQA

ground-water samples had sufficient dissolved oxygen content (> 0.5 mg/L) to be classified as oxic. Finally, the percent volume of MTBE in oxygenated gasoline is generally higher than the percent volume of the gasoline hydrocarbons examined in this report (Canadian Petroleum Products Institute 1994). All of the above properties make it more likely that MTBE will be detected in ground water if released to the environment compared to gasoline hydrocarbons.

The limitation of benzene content in gasoline in the RFG Program has resulted in lower detection frequencies of benzene in ground water in areas of high MTBE use relative to areas of low MTBE use, but has not resulted in lower benzene concentrations. The lower detection frequencies of benzene in ground water in these areas probably also are reflected in source water and drinking water. Because benzene is a known human carcinogen (U.S. Environmental Protection Agency 2000), the lower detection frequencies are a significant change in improving ground-water quality and would be particularly important for drinking-water sources. However, at present (2003) the data for source water and drinking water do not agree with the findings in ground water, which indicates that the influence of the RFG Program on the environmental occurrence of benzene is not completely understood and that more research in this area is warranted.

Associations with MTBE Occurrence

When use of MTBE in gasoline was used as surrogate for input of MTBE to the environment, there was a significant difference in the detection frequency of MTBE between areas of high and low MTBE use. The detection frequency of MTBE was between 5 and 7.5 times higher in areas of high MTBE use compared to areas of low

MTBE use. Previous work has indicated that the detection frequency of MTBE was between 2 and 5 times higher in areas of high MTBE use compared to areas of low MTBE use (Moran et al. 2002). The reason for the greater difference in detection frequencies between areas of high and low MTBE use for ground water as discovered in this report is probably related to other factors, such as population density, which are confounding the analysis. As mentioned, the probability of detecting MTBE is related to population density. Further analysis revealed that, for the ground water survey, population density was higher in the high MTBE use relative to the low MTBE use areas and that this difference was significant ($p < 0.05$; Mann-Whitney test). Thus, the higher population density in areas of high MTBE use relative to areas of low MTBE use probably accounts for the higher difference in the detection frequency ratio reported here.

Nonetheless, it is clear that the use of MTBE in oxygenated gasoline has resulted in higher detection frequencies of MTBE in ground water, source water, and drinking water. In addition, when a comparison was made of the distributions of concentrations of MTBE between areas of high and low MTBE use in ground water, higher concentrations were found in areas of high MTBE use compared to areas of low MTBE use. Thus, ground water underlying areas of high MTBE use has a higher probability of MTBE contamination compared to areas of low MTBE use.

There was no dependence of the detection frequencies of MTBE on dissolved oxygen conditions in ground water when no assessment level was applied. This lack of a dependence of MTBE detection frequencies on dissolved oxygen conditions in ground water seems to support that: 1) MTBE biodegradation occurs in both oxic and anoxic ground water conditions; 2) little MTBE biodegradation occurs in either condition, or 3)

MTBE biodegradation occurs in oxic and/or anoxic ground water conditions but the transformations have no effect on dissolved oxygen concentrations. When an assessment level of 0.5 µg/L was applied to MTBE concentrations, detection frequencies of MTBE were dependent on dissolved oxygen conditions in ground water with a higher detection frequency in anoxic ground water. This result indicates that MTBE biodegradation may be occurring in oxic ground-water conditions for higher MTBE concentrations.

Biodegradation of MTBE has been shown to occur under aerobic biodegradation (Borden et al. 1997; Steffan et al. 1997; Bradley et al. 1999).

After standardizing the estimated coefficients, the results of the logistic regression analyses indicated that three variables are most important in affecting the probability of occurrence of MTBE in ground water. These important variables are population density, use of MTBE in gasoline, and recharge. As population density in the vicinity of the well increased, the probability of detecting MTBE in ground water increased. Likewise, the probability of detecting MTBE in ground water was higher in areas with high use of MTBE in gasoline. Also, as recharge increased the probability of detecting MTBE also increased. Areas of higher population density and higher use of MTBE in gasoline would be expected to be associated with larger numbers of potential point and non-point sources of MTBE to ground water. Higher recharge is likely associated with greater transport of contaminants from the surface to ground water.

The results of the logistic regression analyses also indicated that three other variables affect the probability of occurrence of MTBE in ground water, but have less significance in influencing MTBE occurrence. These three variables are aquifer consolidation, soil permeability, and the density of leaking underground gasoline storage

tanks. The probability of detecting MTBE in ground water was higher in consolidated aquifers compared to unconsolidated aquifers. The effective porosity of consolidated rocks that are fractured is normally very small compared to unconsolidated, granular rocks. However, the average linear velocities of ground water through fractured consolidated materials can be quite high because average linear velocity is inversely proportional to effective porosity (Freeze and Cherry, 1979). Thus, ground water in consolidated aquifers with fracture porosity, such as karst limestone or fractured crystalline rock, moves at a higher velocity relative to unconsolidated aquifers. This means that contaminants that enter consolidated aquifers with fracture porosity can move quickly through the aquifer system and less time is available for attenuation by biodegradation, dispersion, and diffusion.

The probability of detecting MTBE in ground water increased as soil permeability increased. Increased soil permeability likely increases the rate of transfer of contaminants from the surface to ground water. The probability of detecting MTBE in ground water increased with increasing number of leaking underground gasoline storage tanks in the vicinity of the well. Although leaking underground storage tanks might seem to be an important source for MTBE, the standardized coefficient for this variable was the lowest of all variables analyzed. This indicates that, although they may be responsible for some occurrence of MTBE, leaking underground gasoline storage tanks are not the primary source for most MTBE in ground water. Many low concentrations of MTBE in ground water may originate from non-point sources.

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Figures

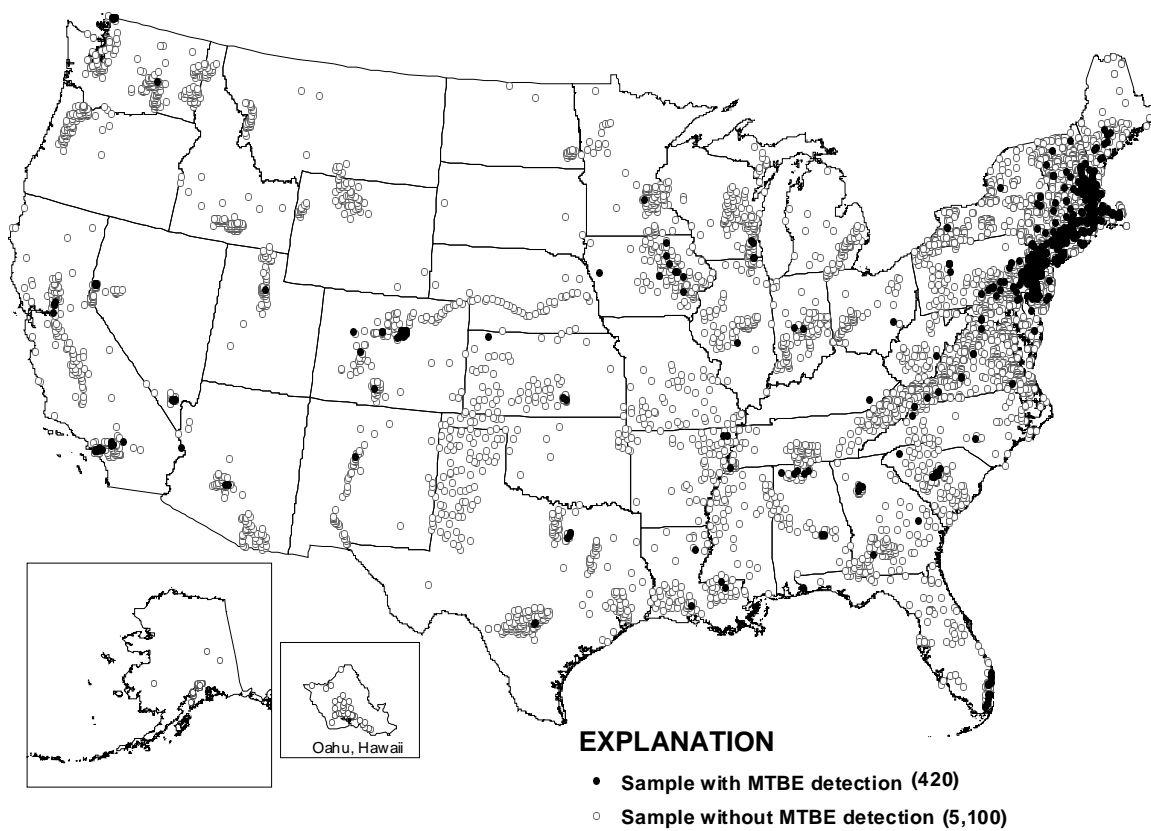


Figure 1. Moran

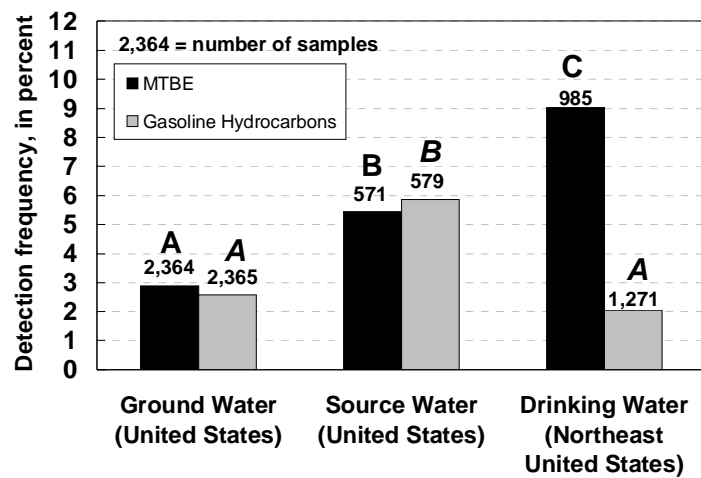


Figure 2. Moran

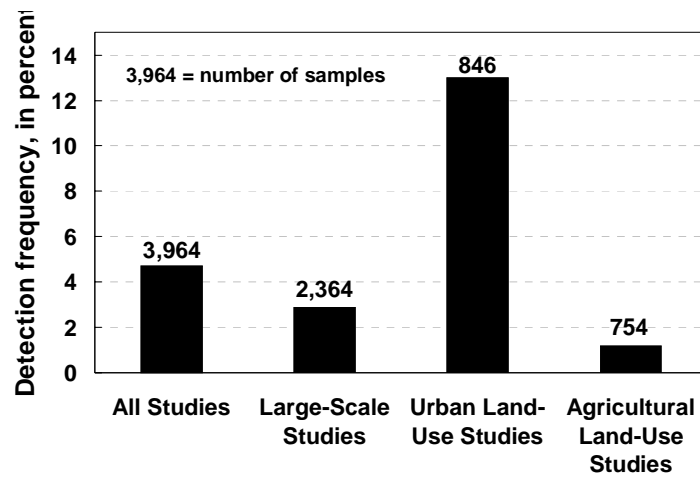


Figure 3. Moran

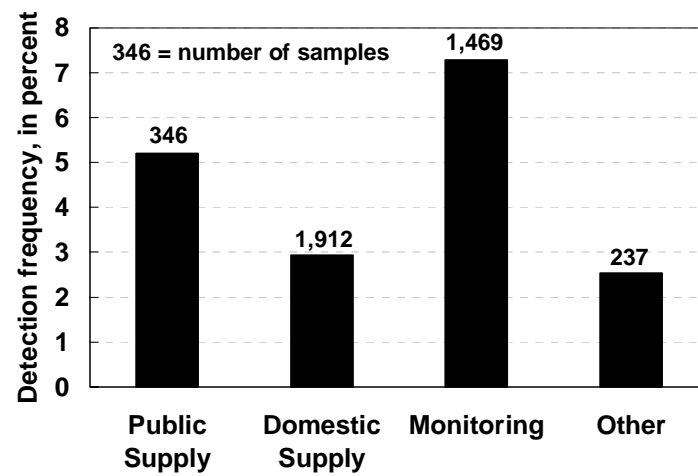


Figure 4. Moran

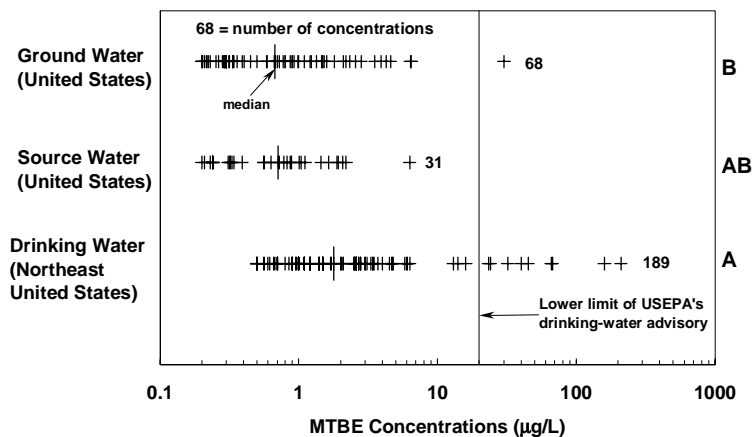


Figure 5. Moran

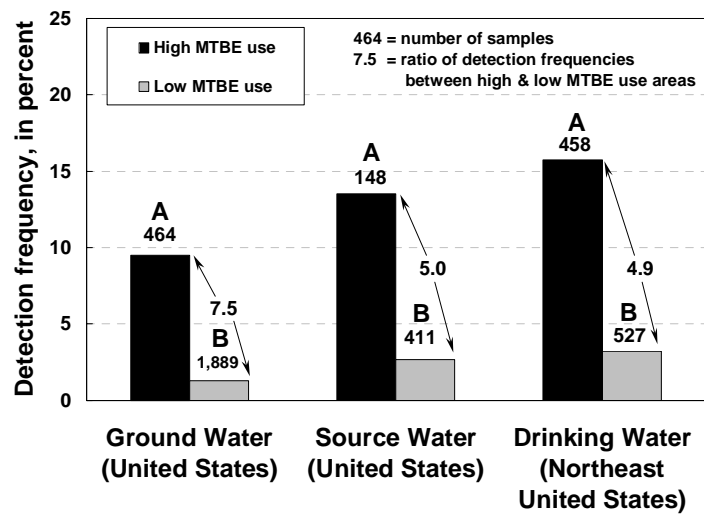


Figure 6. Moran

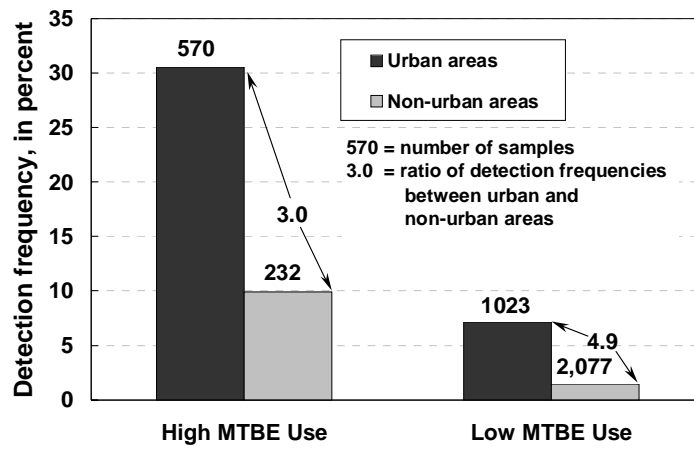


Figure 7. Moran

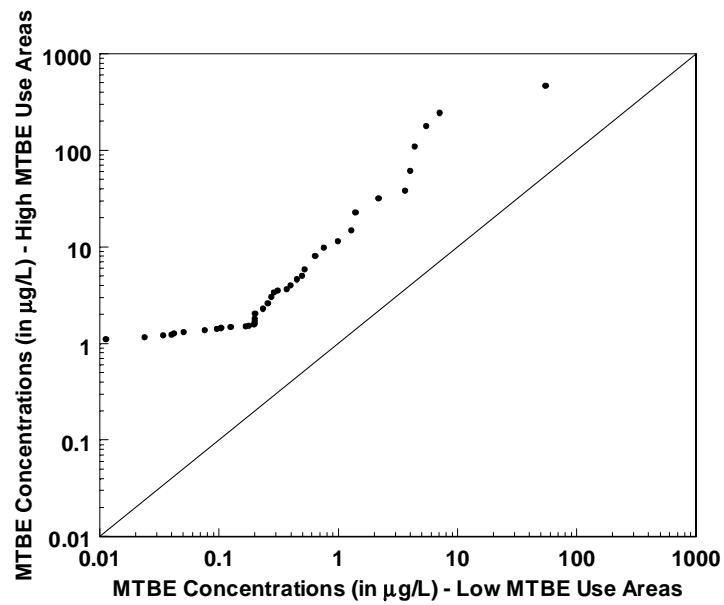


Figure 8. Moran

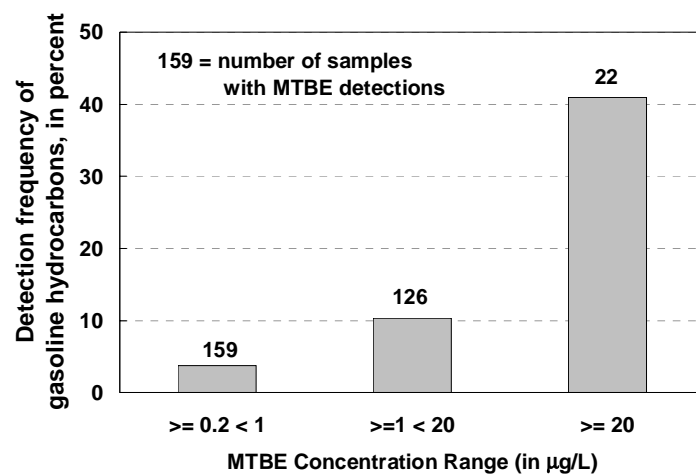


Figure 9. Moran

Table 1			
Anthropogenic and hydrogeologic variables that were used in the logistic regression analysis [GWSI, U.S. Geological Survey Ground Water Site Inventory; USEPA, U.S. Environmental Protection Agency]			
Independent variable	Units	Coding	Source
Anthropogenic Variables			
Use of MTBE in gasoline	None	Binary	U.S. Environmental Protection Agency 2003c; TRW Petroleum Technologies written commun. 1999
Population density	People/km ² (interpolated)	Continuous	Price 2002
Urban land-use area	Percent within 500-m buffer	Continuous	Hitt 2002a
Aboveground storage tanks	Tanks/500 m grid cell (interpolated)	Continuous	C.V. Price, U.S. Geological Survey, written commun. 2003
Underground storage tanks	Tanks/500 m grid cell (interpolated)	Continuous	C.V. Price, U.S. Geological Survey, written commun. 2003
Leaking underground storage tanks	Tanks/500 m grid cell (interpolated)	Continuous	C.V. Price, U.S. Geological Survey, written commun. 2003
Hydrogeologic Variables			
Well depth	Feet	Continuous	GWSI
Depth to the top of the screened interval	Feet	Continuous	GWSI
Water level	Feet below land surface datum	Continuous	GWSI
Land surface slope	Percent	Continuous	Hitt 2002b
Depth to seasonal high water table in soil	Inches	Continuous	Hitt 2002b
Soil permeability	Inches/hour	Continuous	Hitt 2002b
Soil organic matter content	Percent by weight	Continuous	Hitt 2002b
Soil clay content	Percent	Continuous	Hitt 2002b
Aquifer confinement	None	Categorical	GWSI
Aquifer consolidation	None	Binary	GWSI
Recharge	mm/year	Continuous	D.M. Wolock, U.S. Geological Survey, written commun. 2003

Moran

<p>Table 2</p> <p>Anthropogenic and hydrogeologic variables that were significantly associated with the probability of detecting MTBE in ground water (Wald statistic p-value < 0.05)</p>			
Independent variable	Unstandardized estimated coefficient	Standardized estimated coefficient	Odds ratio
Anthropogenic Variables			
Population density	0.367	0.24	1.4
Use of MTBE in gasoline	1.762	0.21	5.8
Leaking underground storage tanks	0.463	0.04	1.6
Hydrogeologic Variables			
Recharge	0.005	0.17	1.0
Aquifer consolidation	-0.582	-0.08	0.6
Soil permeability	0.043	0.05	1.0

Moran

Figure Captions:

- Figure 1.** Location of samples of ground water, source water, and drinking water that were analyzed for MTBE and the locations of samples with detections of MTBE using no assessment level.
- Figure 2.** Detection frequency of MTBE or any gasoline hydrocarbon in samples of ground water, source water, or drinking water using an assessment level of 0.2 µg/L.
- Figure 3.** Detection frequency of MTBE in samples from various NAWQA occurrence studies using no assessment level.
- Figure 4.** Detection frequency of MTBE in samples from various well types (NAWQA studies) using no assessment level.
- Figure 5.** MTBE concentrations in samples of ground water, source water, and drinking water using an assessment level of 0.2 µg/L.
- Figure 6.** Detection frequency of MTBE in samples of ground water, source water, and drinking water for areas of high and low MTBE use using an assessment level of 0.2 µg/L.
- Figure 7.** Detection frequency of MTBE in samples of ground water for areas of urban and non-urban land use and by areas of high and low MTBE use using no assessment level.
- Figure 8.** Distribution of concentrations of MTBE in ground water for areas of high and low MTBE use using no assessment level.
- Figure 9.** Detection frequency of any gasoline hydrocarbon in samples of ground water for selected concentration ranges of MTBE using an assessment level of 0.2 µg/L.